Senegoses J—O, Oligosaccharide Multi-Esters from the Roots of *Polygala senega* L.

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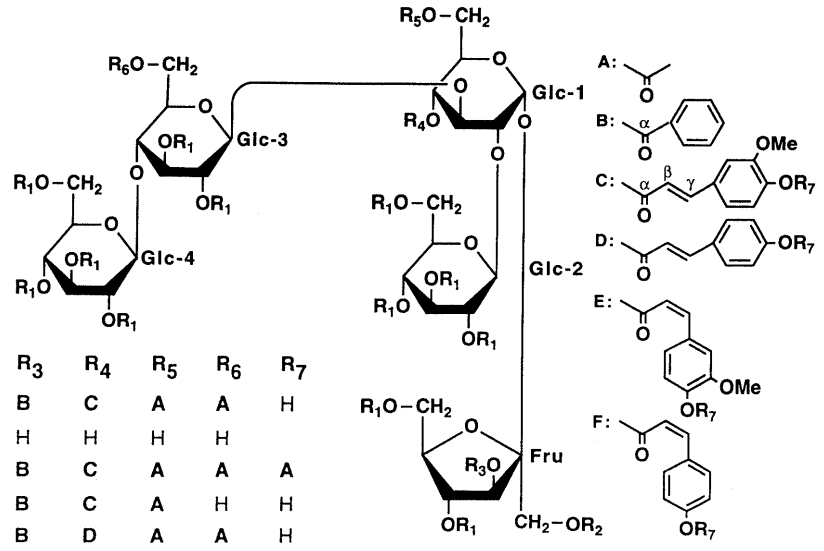
From the roots of *Polygala senega* L. six new oligosaccharides, called senegoses J—O, were isolated and their structures were elucidated by spectroscopic and chemical means. These oligosaccharides were esterified with acetic, benzoic, *p*-coumaric and ferulic acids.

Keywords *Polygala senega*; senegose; acylated oligosaccharide; Polygalaceae; pentasaccharide

In previous papers,[1,2] we reported the isolation and structural elucidation of nine new oligosaccharide multi-esters called senegoses A—I from the roots of *Polygala senega* var. *latifolia* TORR. *et* GRAY (Polygalaceae). The rarity of the structure prompted us to investigate further for additional oligosaccharide constituents of *Polygala senega* L. and we have been successful in isolating other new oligosaccharide multi-esters. This paper reports the isolation and structural elucidation of these rare oligosaccharides called senegoses J—O. All of them gave the same pentasaccharide **1a** which was identical to the deacyl compound of senegoses A—E on alkaline hydrolysis,[1] suggesting that senegoses J—O were homologous to senegoses A—E.

Senegose J (**1**), $[\alpha]_D$ −6.6°, $C_{60}H_{74}O_{34}\cdot 4H_2O$ was obtained as an amorphous powder and it exhibited $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 1361 and 1339, respectively, under FAB-MS. On acid hydrolysis compound **1** gave glucose and fructose in the ratio 4 : 1, while on alkaline hydrolysis it gave a pentasaccharide **1a** and acid mixture composed of benzoic, *p*-coumaric and ferulic acid (see Experimental). On acetylation, **1** afforded a peracetate **1b** which exhibited two aromatic [δ 2.24, 2.33 (each 3H, s)] and fourteen aliphatic [δ 1.77, 1.95, 1.981, 1.983, 2.02, 2.056, 2.07, 2.081, 2.084, 2.10 (each 3H, s), 1.96, 2.063 (each 6H, s)] acetoxyl signals in the ^{1}H-NMR spectrum. In the NMR spectrum of **1**, two acetyl, one benzoyl, one *p*-coumaroyl and one feruloyl signal were observed (see Tables I and II). Detailed proton spin decoupling experiments which started from the irradiation at each anomeric proton signal and differential nuclear Overhauser effect (NOE) experiments involving irradiation at each anomeric proton signal enabled us to assign all proton signals of the Glc-1 and Glc-3 moieties (see Chart 2 and Table I). The C–H COSY spectrum and above mentioned ^{1}H-NMR data led us to assume that the sugar linkage and the acylated sites of senegose J (**1**) are as shown. The position of each acyl residue was allocated by observation of $^3J_{(COCH)}$ using the ^{1}H detected heteronuclear multiple bond connectivity (HMBC) method and NOE



	R_1	R_2	R_3	R_4	R_5	R_6	R_7
1	H	D	B	C	A	A	H
1a	H	H	H	H	H	H	
1b	A	D	B	C	A	A	A
2	H	D	B	C	A	H	H
3	H	C	B	D	A	A	H
3b	A	C	B	D	A	A	A
4	H	C	B	D	A	H	H
5	H	D	B	E	A	A	H
6	H	F	B	C	A	A	H

Chart 1

TABLE I. ^{1}H-NMR Data for Oligosaccharides from the Roots of *Polygala senega* in MeOH-d_4

	1	2	3	4	5	6
Glc-1						
1	5.86 (1H, d, J=3.5 Hz)	5.85 (1H, d, J=3.5 Hz)	5.86 (1H, d, J=3.5 Hz)	5.86 (1H, d, J=8 Hz)	5.83 (1H, d, J=8 Hz)	5.85 (1H, d, J=8 Hz)
2	3.82 (1H, dd, J=9.5, 3.5 Hz)	3.81 (1H, dd, J=9.5, 3.5 Hz)	3.82 (1H, dd, J=9.5, 3.5 Hz)	3.81 (1H, dd, J=9.5, 3.5 Hz)	3.81 (1H, dd, J=9.5, 3.5 Hz)	3.82 (1H, dd, J=9.5, 3.5 Hz)
3	3.95 (1H, t, J=9.5 Hz)	3.99 (1H, t, J=9.5 Hz)	3.95 (1H, t, J=9.5 Hz)	3.98 (1H, t, J=9.5 Hz)	3.89 (1H, t, J=9.5 Hz)	3.96 (1H, t, J=9.5 Hz)
4	5.02 (1H, t, J=9.5 Hz)	5.00 (1H, dd, J=10, 9.5 Hz)	5.00 (1H, d, J=9.5 Hz)	5.00 (1H, t, J=9.5 Hz)	4.98 (1H, t, J=9.5 Hz)	5.01 (1H, t, J=9.5 Hz)
5	4.38 (1H, m)	4.39 (1H, m)	4.39 (1H, m)	4.39 (1H, m)	4.36 (1H, m)	4.37 (1H, m)
6	4.15 [a]	4.14 (1H, dd, J=12, 6 Hz)	4.13 [a]	4.14 (1H, dd, J=12, 6 Hz)	4.14 [a]	4.13 [a]
	4.19 (1H, dd, J=12,3 Hz)	4.20 (1H, dd, J=12, 3 Hz)	4.18 (1H, dd, J=12, 3 Hz)	4.20 (1H, dd, J=12, 3 Hz)	4.19 (1H, dd, J=12, 3 Hz)	4.18 [a]
Glc-2						
1	4.60 (1H, d, J=8 Hz)	4.59 (1H, d, J=8 Hz)	4.60 (1H, d, J=8 Hz)	4.59 (1H, d, J=8 Hz)	4.60 (1H, d, J=8 Hz)	4.59 (1H, d, J=8 Hz)
Glc-3						
1	4.56 (1H, d, J=8 Hz)	4.48 (1H, d, J=8 Hz)	4.55 (1H, d, J=8 Hz)	4.46 (1H, d, J=8 Hz)	4.50 (1H, d, J=8 Hz)	4.56 (1H, d, J=8 Hz)
2	3.08 (1H, t, J=8 Hz)	3.08 (1H, t, J=8 Hz)	3.08 (1H, t, J=8 Hz)	3.09 (1H, t, J=8 Hz)	3.09 (1H, t, J=8 Hz)	3.07 (1H, t, J=8 Hz)
3	3.35 (1H, t, J=8 Hz)	3.34 (1H, t, J=8 Hz)	3.35 (1H, t, J=8 Hz)	3.35 [a]	3.35 (1H, t, J=8 Hz)	3.35 (1H, t, J=8 Hz)
4	3.42 (1H, t, J=8 Hz)	3.39 (1H, t, J=8 Hz)	3.42 (1H, t, J=8 Hz)	3.41 (1H, t, J=8 Hz)	3.38 (1H, t, J=8 Hz)	3.42 (1H, t, J=8 Hz)
5	3.25 (1H, m)	3.13 (1H, m)	3.22 [a]	3.10 [a]	3.25 (1H, m)	3.28 [a]
6	4.15 [a]	3.59 [a]	4.09 (1H, dd, J=12, 3 Hz)	3.56 (1H, dd, J=12, 2 Hz)	4.10 (1H, dd, J=12, 3.5 Hz)	4.14 [a]
			4.13 [a]			4.18 [a]
Glc-4						
1	4.15 (1H, d, J=8 Hz)	4.28 (1H, d, J=8 Hz)	4.15 (1H, d, J=8 Hz)	4.29 (1H, d, J=8 Hz)	4.14 (1H, d, J=8 Hz)	4.14 (1H, d, J=8 Hz)
Fru						
1	4.18 (1H, d, J=12 Hz)	4.17 (1H, d, J=12 Hz)	4.18 (1H, d, J=12 Hz)	4.19 (1H, d, J=12 Hz)	4.17 (1H, d, J=12 Hz)	4.11 (1H, d, J=12 Hz)
	4.69 (1H, d, J=12 Hz)	4.70 (1H, d, J=12 Hz)	4.70 (1H, d, J=12 Hz)	4.71 (1H, d, J=12 Hz)	4.69 (1H, d, J=12 Hz)	4.67 (1H, d, J=12 Hz)
3	5.73 (1H, d, J=8 Hz)	5.74 (1H, d, J=8 Hz)	5.74 (1H, d, J=8 Hz)	5.74 (1H, d, J=8 Hz)	5.73 (1H, d, J=8 Hz)	5.61 (1H, d, J=8 Hz)
4	4.42 (1H, t, J=8 Hz)	4.42 (1H, t, J=8 Hz)	4.43 (1H, t, J=8 Hz)	4.43 (1H, t, J=8 Hz)	4.41 (1H, t, J=8 Hz)	4.39 (1H, t, J=8 Hz)
5	4.07 (1H, m)	4.07 (1H, m)	4.08 (1H, m)	4.08 (1H, m)	4.07 (1H, m)	4.11 (1H, m)
6	3.82 [a]		3.83 [a]	3.85 [a]	3.84 [a]	3.96 [a]
	3.86 [a]		3.89 [a]	3.89 [a]		
Ac (R_5)						
2	2.06 (3H, s)	2.07 (3H, s)	2.06 (3H, s)	2.07 (3H, s)	2.04 (3H, s)	2.06 (3H, s)
Ac (R_6)						
2	1.57 (3H, s)		1.59 (3H, s)		1.83 (3H, s)	1.56 (3H, s)
Bz (R_3)						
2, 6	8.18 (2H, dd, J=8, 1 Hz)	8.17 (2H, dd, J=8, 1 Hz)	8.18 (2H, dd, J=8, 1 Hz)	8.17 (2H, dd, J=8, 1 Hz)	8.14 (2H, dd, J=8, 1 Hz)	8.16 (2H, dd, J=8, 1 Hz)
3, 5	7.62 (2H, t, J=8 Hz)	7.57 (2H, t, J=8 Hz)	7.61 (2H, t, J=8 Hz)	7.57 (2H, t, J=8 Hz)	7.58 (2H, t, J=8 Hz)	7.61 (2H, t, J=8 Hz)
4	7.72 (1H, tt, J=8, 1 Hz)	7.64 (1H, tt, J=8, 1 Hz)	7.73 (1H, tt, J=8, 1 Hz)	7.66 (1H, tt, J=8, 1 Hz)	7.73 (1H, tt, J=8, 1 Hz)	7.71 (1H, tt, J=8, 1 Hz)
Cinn (R_2)						
2	7.43 (1H, d, J=8.5 Hz)	7.43 (1H, d, J=8.5 Hz)	7.20 (1H, d, J=2 Hz)	7.19 (1H, d, J=2 Hz)	7.42 (1H, d, J=8.5 Hz)	7.67 (1H, d, J=8.5 Hz)
3	6.81 (1H, d, J=8.5 Hz)	6.80 (1H, d, J=8.5 Hz)			6.81 (1H, d, J=8.5 Hz)	6.78 (1H, d, J=8.5 Hz)
5	6.81 (1H, d, J=8.5 Hz)	6.80 (1H, d, J=8.5 Hz)	6.81 (1H, d, J=8 Hz)	6.81 (1H, d, J=8 Hz)	6.81 (1H, d, J=8.5 Hz)	6.78 (1H, d, J=8.5 Hz)
6	7.43 (1H, d, J=8.5 Hz)	7.43 (1H, d, J=8.5 Hz)	7.00 (1H, dd, J=8, 2 Hz)	7.02 (1H, dd, J=8, 2 Hz)	7.42 (1H, d, J=8.5 Hz)	7.67 (1H, d, J=8.5 Hz)
β	6.37 (1H, d, J=16 Hz)	6.36 (1H, d, J=16 Hz)	6.42 (1H, d, J=16 Hz)	6.41 (1H, d, J=16 Hz)	6.36 (1H, d, J=16 Hz)	5.87 (1H, d, J=13 Hz)
γ	7.68 (1H, d, J=16 Hz)	7.68 (1H, d, J=16 Hz)	7.68 (1H, d, J=16 Hz)	7.67 (1H, d, J=16 Hz)	7.67 (1H, d, J=16 Hz)	6.90 (1H, d, J=13 Hz)
OMe			3.90 (3H, s)	3.90 (3H, s)		
Cinn (R_4)						
2	7.22 (1H, d, J=2 Hz)	7.21 (1H, d, J=2 Hz)	7.46 (1H, d, J=8.5 Hz)	7.48 (1H, d, J=8.5 Hz)	7.74 (1H, d, J=2 Hz)	7.23 (1H, d, J=2 Hz)
3			6.86 (1H, d, J=8.5 Hz)	6.86 (1H, d, J=8.5 Hz)		
5	6.85 (1H, d, J=8 Hz)	6.87 (1H, d, J=8 Hz)	6.86 (1H, d, J=8.5 Hz)	6.86 (1H, d, J=8.5 Hz)	6.78 (1H, d, J=8 Hz)	6.84 (1H, d, J=8 Hz)
6	7.05 (1H, dd, J=8, 2 Hz)	7.09 (1H, dd, J=8, 2 Hz)	7.46 (1H, d, J=8.5 Hz)	7.48 (1H, d, J=8.5 Hz)	7.14 (1H, dd, J=8, 2 Hz)	7.05 (1H, dd, J=8, 2 Hz)
β	6.24 (1H, d, J=16 Hz)	6.32 (1H, d, J=16 Hz)	6.21 (1H, d, J=16 Hz)	6.29 (1H, d, J=16 Hz)	5.66 (1H, d, J=13 Hz)	6.24 (1H, d, J=16 Hz)
γ	7.57 (1H, d, J=16 Hz)	7.58 (1H, d, J=16 Hz)	7.57 (1H, d, J=16 Hz)	7.58 (1H, d, J=16 Hz)	6.82 (1H, d, J=13 Hz)	7.56 (1H, d, J=16 Hz)
OMe	3.97 (3H, s)	3.92 (3H, s)			3.86 (3H, s)	3.96 (3H, s)

Recorded on a JEOL GSX-500 (500 MHz). *a*) Overlapping with other signals.

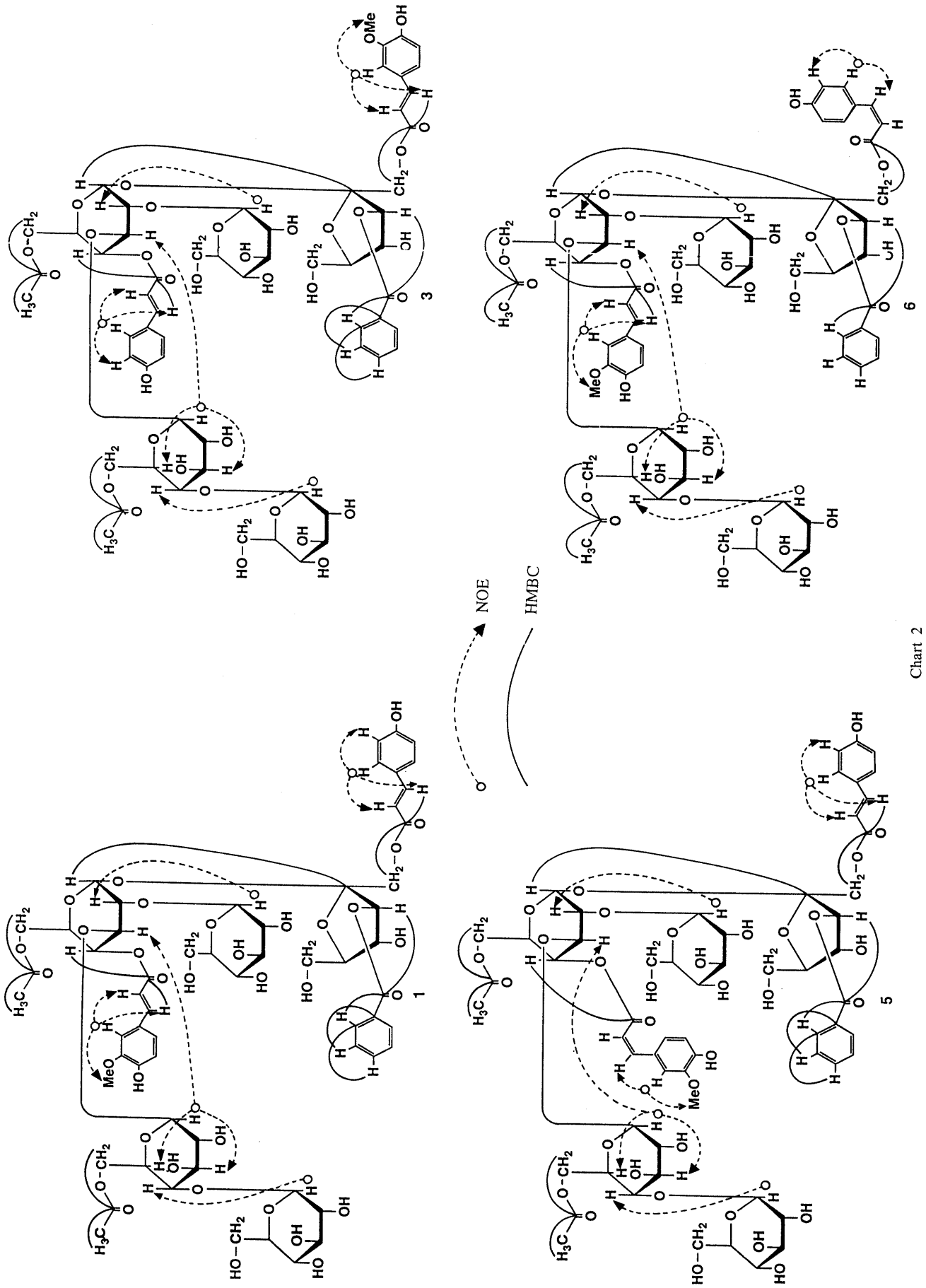


Chart 2

experiments (see Chart 2).[3] The carbon signals of the ester moiety were assigned from the HMBC (see Chart 2 and Table II). The details are as follows. NOEs were observed at the signals δ 3.97 (3H, s), 6.24 (1H, d, $J=16$ Hz) and 7.57 (1H, d, $J=16$ Hz) on irradiation at the signal δ 7.22 (1H, d, $J=2$ Hz), suggesting these signals were assigned to feruloyl residue (see Chart 2). The $^3J_{(CCCH)}$ was observed between an ester carbonyl carbon signal (δ 167.9) and an olefinic γ-proton signal (δ 7.57), and $^3J_{(COCH)}$ between the carbonyl carbon signal and H-4 of Glc-1. So, the feruloyl residue was located at C-4 of Glc-1. These data led us to assign the structure of **1** to senegose J. The glycosylation and acylation shifts in the ^{13}C-NMR spectrum of senegose J supported this conclusion.

The ^{1}H-NMR spectrum of senegose K (**2**), $[\alpha]_D$ $-2.6°$, $C_{58}H_{72}O_{33}\cdot 3H_2O$ showed that this compound was composed of a pentasaccharide **1a**, one acetic, one benzoic, one *p*-coumaric and one ferulic acid. On acetylation, this compound gave the peracetate **1b** and a pentasaccharide **1a** on alkaline hydrolysis as in the case of **1**. Therefore, the positions of the benzoyl, *p*-coumaroyl and feruloyl groups were the same as in **1**. Comparing the ^{1}H- and ^{13}C-NMR spectra with those of **1**, an acetyl methyl signal was observed at δ 2.07, the H-6 of Glc-3 were shifted upfield to δ 3.59 (Δ -0.56 ppm), the C-5 of Glc-3 was shifted downfield to δ 75.9 (Δ $+2.7$ ppm) and the C-6 of Glc-3 upfield to δ 62.3 (Δ -1.7 ppm) in **2**. Therefore, the structure of senegose K was assigned as **2**.

Senegose L (**3**), $[\alpha]_D$ $-6.3°$, $C_{60}H_{74}O_{34}\cdot 4H_2O$ was obtained as an amorphous powder and it exhibited $[M+Na]^+$ and $[M+H]^+$ ions at *m/z* 1361 and 1339, respectively, under FAB-MS. The ^{1}H-NMR spectrum showed the presence of two acetyl groups, one benzoyl, one *p*-coumaroyl and one feruloyl group (see Table I). Compound **3** gave glucose and fructose in the ratio 4:1 on acid hydrolysis, while alkaline hydrolysis gave a pentasaccharide **1a** and an acid mixture composed of benzoic, *p*-coumaric and ferulic acids (see Experimental). On acetylation **3** gave a peracetate **3b** and its ^{1}H-NMR spectrum showed the presence of two aromatic [δ 2.33 (6H, s)] and fourteen aliphatic acetoxyl signals [δ 1.78, 1.956, 1.98, 2.02, 2.06, 2.08, 2.10, 2.23 (3H, s), 1.96, 2.065, 2.072, (6H, s)]. The position of each acyl residue was decided by observation of ^2J and ^3J using HMBC and NOE experiments (see Chart 2). These data led us to assign the structure of **3** to senegose L.

The ^{1}H-NMR spectrum of senegose M (**4**), $[\alpha]_D$ $+4.4°$, $C_{58}H_{72}O_{33}\cdot 5H_2O$ showed that this compound was composed of a pentasaccharide **1a**, one benzoic, one *p*-coumaric and one ferulic and two acetic acid moieties. H_2-6 of Glc-3 were shifted upfield to δ 3.56 (Δ -0.57 ppm) compared with those of **3**. On acetylation this compound gave the peracetate **3b** as in the case of **3**. So, the structure of senegose M was assigned as **4**.

Senegose N (**5**), $[\alpha]_D$ $+39.6°$, $C_{60}H_{74}O_{34}\cdot 5H_2O$ was obtained as an amorphous powder and it showed $[M+Na]^+$ ion at *m/z* 1361 in FAB-MS. The ^{1}H-NMR spectrum showed the presence of two acetyl groups, one benzoyl, one *p*-coumaroyl and one *cis*-feruloyl group (see Table I). Compound **5** gave glucose and fructose in the ratio 4:1 on acid hydrolysis, while alkaline hydrolysis

TABLE II. ^{13}C-NMR Data for Oligosaccharides from the Roots of *Polygala senega* in MeOH-d_4

	1	**2**	**3**	**4**	**5**	**6**
Glc-1						
1	92.9	92.8	92.9	92.8	92.9	92.9
2	81.4	81.5	81.4	81.3	81.2	81.4
3	78.8	79.6	78.8	79.6	79.6	78.8
4	70.2	70.8	70.3	70.9	70.0	70.2
5	69.6	69.6	69.6	69.6	69.5	69.6
6	64.3	64.4	64.3	64.4	64.5	64.3
Glc-2						
1	105.3	105.4	105.3	105.4	105.3	105.3
2	75.3	75.3	75.3	75.2	75.3	75.4
3	78.5	78.5	78.5	78.3	78.6	78.6
4	71.6	71.6	71.6	71.6	71.6	71.7
5	78.1	78.0	78.1	77.9	78.1	78.1
6	63.0	63.0	63.0	63.0	63.0	63.1
Glc-3						
1	104.0	104.4	104.0	104.5	104.2	104.0
2	75.1	75.3	75.1	75.2	75.3	75.2
3	76.3	76.2	76.2	76.1	76.2	76.3
4	80.6	80.9	80.7	80.9	80.8	80.7
5	73.2	75.9	73.2	75.8	73.2	73.3
6	64.0	62.3	64.0	62.3	64.4	64.0
Glc-4						
1	104.7	104.5	104.7	104.7	104.8	104.7
2	74.7	74.8	74.7	74.7	74.7	74.7
3	78.4	78.3	78.4	78.4	78.4	78.4
4	71.3	71.3	71.3	71.2	71.3	71.4
5	77.8	77.8	77.8	77.7	77.8	77.8
6	62.4	62.4	62.4	62.3	62.4	62.4
Fru						
1	65.8	65.7	65.9	65.8	65.8	65.5
2	103.9	103.9	103.9	103.9	103.9	103.8
3	80.0	80.0	80.1	80 0	80.0	79.8
4	73.9	74.0	74.0	74.0	74.0	73.6
5	84.6	84.7	84.7	84.7	84.7	84.4
6	63.8	63.8	63.9	63.8	63.8	63.7
Ac (R_5)						
1	172.5	172.5	172.5	172.5	172.4	172.5
2	20.8	20.8	20.8	20.8	21.0	20.8
Ac (R_6)						
1	172.4		172.4		172.7	172.4
2	20.5		20.6		20.7	20.5
Bz (R_3)						
1	130.9	130.9	130.9	130.8	130.8	130.9
2, 6	131.0	131.1	131.0	131.0	130.9	131.0
3, 5	130.0	129.9	130.0	129.9	130.0	129.9
4	134.9	134.8	135.0	134.8	135.0	134.9
α	167.2	167.2	167.2	167.2	167.2	167.2
Cinn (R_2)						
1	127.1	127.0	127.7	127.7	127.1	127.5
2	131.2	131.3	111.6	111.6	131.3	133.7
3	116.9	116.9	149.4	149.4	116.9	116.9
4	161.3	161.5	150.5	150.6	161.4	160.2
5	116.9	116.9	116.5	116.5	116.9	116.9
6	131.2	131.3	124.4	124.4	131.3	133.7
α	168.4	168.4	168.4	168.4	168.4	167.6
β	114.8	114.7	115.2	115.1	114.8	116.0
γ	147.0	147.1	147.3	147.1	147.0	145.3
OMe			56.5	56.5		
Cinn (R_4)						
1	127.4	127.4	127.0	127.6	127.8	127.4
2	111.5	111.8	131.4	131.4	115.3	111.6
3	149.4	149.5	117.0	116.9	148.4	149.5
4	150.9	151.1	161.5	161.4	149.8	151.0
5	116.5	116.6	117.0	116.9	116.3	116.5
6	124.7	124.4	131.4	131.4	127.0	124.7
α	167.9	168.0	167.9	168.0	166.7	168.0
β	115.0	115.3	114.8	115.1	115.7	115.0
γ	147.3	147.4	147.0	147.3	145.9	147.3
OMe	56.4	56.5			56.6	56.4

Recorded on a JEOL GSX-270 (67.80 MHz).

gave a pentasaccharide **1a** and an acid mixture composed of benzoic, *p*-coumaric and *cis*-ferulic acids (see Experimental). The position of each acyl residue was determined by observation of ^2J and ^3J using HMBC and NOE experiments, except for the *cis*-feruloyl group. The $^3J_{(CCCH)}$ between an ester carbonyl carbon signal and an olefinic-γ-proton signal (δ 6.82) of *cis*-feruloyl group was not observed in the HMBC spectrum (see Chart 2). But H-4 of Glc-1 was shifted downfield to δ 4.98 and the only residual acyl residue was the *cis*-feruloyl group. This group was therefore determined at C-4 of Glc-1. These data led us to assign the structure of **5** to senegose N.

The ^{1}H-NMR spectrum of senegose O (**6**), $[\alpha]_D$ $-13.0°$, $C_{60}H_{74}O_{34}\cdot 4H_2O$ showed that this compound was composed of a pentasaccharide **1a**, one benzoic, one *cis*-*p*-coumaric, one ferulic and two acetic acids. The position of each acyl group was determined by observation of ^2J and ^3J using HMBC and NOE experiments, except for the *cis*-*p*-coumaroyl group. The ^3J between an ester carbonyl carbon signal and an olefinic-γ-proton signal (δ 6.90) of *cis*-*p*-coumaroyl group also was not observed (see Chart 2). But H_2-1 of Fru were shifted downfield, so the *cis*-*p*-coumaroyl group was determined at C-1 of Fru. These data led us to assign the structure of **6** to senegose O.

The anomeric configuration of Glc-1, Glc-2, Glc-3 and Glc-4 was determined to be α, β, β and β, respectively, from each $^3J_{H_1-H_2}$ value, and that of the Fru moiety was determined to be β from the NOE experiment described below. When the signals due to the H-3 of Fru were irradiated, NOEs were observed at those due to the H_2-1 of Fru. The absolute configuration of each monosaccharide was not determined.

Experimental

General Procedure Instrumental analyses were carried out as described previously.[4]

Isolation *Polygala senega* L. (imported from Canada) (2.8 kg) was extracted twice with hot water. The extract was passed through a Mitsubishi Diaion HP-20 column (9 cm × 80 cm) and the adsorbed material eluted with 50% MeOH aq., 70% MeOH aq. and MeOH successively to give a pale yellow powder (50% MeOH aq. eluate 159 g, 70% MeOH aq. eluate 102 g and MeOH eluate 96 g). The 70% MeOH aq. eluate was chromatographed on a silica gel (1020 g) column using $CHCl_3$–MeOH (75 : 25) as a mobile phase to give fractions 1 (1.2 g), 2 (0.4 g), 3 (11.5 g), 4 (7.6 g), 5 (4.0 g), 6 (24.5 g), 7 (5.0 g), 8 (4.8 g), 9 (2.7 g), 10 (2.4 g), 11 (0.9 g), 12 (20.1 g), 13 (14.2 g), 14 (1.1 g), 15 (0.6 g). From fractions 8 and 9, oligosaccharides were isolated by preparative HPLC [Develosil Lop-ODS 5 cm × 50 cm × 2, CH_3CN–H_2O (22.5 : 77.5)]: **1** (72 mg), **2** (91 mg), **3** (18 mg), **4** (52 mg), **5** (19 mg), **6** (13 mg).

Senegose J (1) Amorphous powder. $[\alpha]_D^{25}$ $-6.6°$ (c = 1.13, MeOH). UV λ_{max}^{MeOH} nm (log ε): 224 (4.44), 231 (4.48), 288 (sh 4.36), 303 (sh 4.49), 320 (4.58). *Anal.* Calcd for $C_{60}H_{74}O_{34}\cdot 4H_2O$: C, 51.06; H, 5.86. Found: C, 51.11; H, 5.83. FAB-MS *m/z*: 1361 $[M+Na]^+$, 1339 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose K (2) Amorphous powder. $[\alpha]_D^{25}$ $-2.6°$ (c = 0.97, MeOH). UV λ_{max}^{MeOH} nm (log ε): 223 (4.43), 231 (4.46), 287 (sh 4.32), 302 (sh 4.45), 319 (4.53). *Anal.* Calcd for $C_{58}H_{72}O_{33}\cdot 3H_2O$: C, 51.55; H, 5.82. Found: C, 51.73; H, 5.93. FAB-MS *m/z*: 1319 $[M+Na]^+$, 1297 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose L (3) Amorphous powder. $[\alpha]_D^{25}$ $-6.3°$ (c = 1.03, MeOH). UV λ_{max}^{MeOH} nm (log ε): 222 (4.36), 232 (4.40), 286 (sh 4.23), 302 (sh 4.37). *Anal.* Calcd for $C_{60}H_{74}O_{34}\cdot 4H_2O$: C, 51.06; H, 5.86. Found: C, 51.29; H, 5.76. FAB-MS *m/z*: 1361 $[M+Na]^+$, 1339 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose M (4) Amorphous powder. $[\alpha]_D^{25}$ $+4.4°$ (c = 0.57, MeOH). UV λ_{max}^{MeOH} nm (log ε): 223 (4.51), 232 (4.54), 287 (sh 4.36), 302 (sh 4.47), 320 (4.56). *Anal.* Calcd for $C_{58}H_{72}O_{33}\cdot 5H_2O$: C, 50.22; H, 5.96. Found: C, 50.46; H, 5.93. FAB-MS *m/z*: 1319 $[M+Na]^+$, 1297 $[M+H]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose N (5) Amorphous powder. $[\alpha]_D^{25}$ $+39.6°$ (c = 0.82, MeOH). UV λ_{max}^{MeOH} nm (log ε): 224 (4.38), 230 (4.40), 286 (sh, 4.27), 302 (sh 4.40), 318 (4.48). *Anal.* Calcd for $C_{60}H_{74}O_{34}\cdot 5H_2O$: C, 50.42; H, 5.72. Found: C, 50.69; H, 5.83. FAB-MS *m/z*: 1361 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Senegose O (6) Amorphous powder. $[\alpha]_D^{25}$ $-13.1°$ (c = 0.73, MeOH). UV λ_{max}^{MeOH} nm (log ε): 220 (3.43), 230 (3.42), 286 (sh 3.24), 301 (sh 3.35), 320 (3.42). *Anal.* Calcd for $C_{60}H_{74}O_{34}\cdot 4H_2O$: C, 51.06; H, 5.86. Found: C, 51.14; H, 5.93. FAB-MS *m/z*: 1361 $[M+Na]^+$. ^{1}H- and ^{13}C-NMR: Tables I and II.

Acetylation of 1—4 A sample of each compound (3 mg) was treated with acetic anhydride–pyridine (1 : 1) (3 drops) overnight at 35°C and the reagents were then evaporated to give a residue. From **1** and **2**, **1b** was obtained as an amorphous powder. **1b**: ^{1}H-NMR ($CDCl_3$): δ 1.77, 1.95, 1.981, 1.983, 2.02, 2.056, 2.07, 2.081, 2.084, 2.10 (each 3H, s, aliphatic OAc), 1.96, 2.063 (each 6H, s, aliphatic OAc), 2.33, 2.34 (each 3H, s, aromatic OAc), 3.93 (3H, s, OMe), 4.38, 4.43, 4.64 (each 1H, d, J = 8 Hz, H-1 of Glc), 5.68 (1H, d, J = 3.5 Hz, H-1 of Glc-1), 6.28 (1H, d, J = 16 Hz, H-β of fer.), 6.51 (1H, d, J = 16 Hz, H-β of *p*-coum.), 7.10 (1H, d, J = 8 Hz, H-5 of fer.), 7.14 (2H, d, J = 8.5 Hz, H-3, H-5 of *p*-coum.), 7.15 (1H, dd, J = 8, 2 Hz, H-6 of fer.), 7.22 (1H, d, J = 2 Hz, H-2 of fer.), 7.49 (2H, t, J = 8 Hz, H-3, H-5 of benz.), 7.59 (2H, d, J = 8.5 Hz, H-2, H-6 of *p*-coum.), 7.61 (1H, tt, J = 8, 1 Hz, H-4 of benz.), 7.64 (1H, d, J = 16 Hz, H-γ of fer.), 7.79 (1H, d, J = 16 Hz, H-γ of *p*-coum.), 8.10 (2H, dd, J = 8, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 1950 $[M+Na]^+$, 1928 $[M+H]^+$. From **3** and **4**, **3b** was obtained as an amorphous powder. **3b**: ^{1}H-NMR ($CDCl_3$): δ 1.78, 1.956, 1.98, 2.02, 2.06, 2.08, 2.10, 2.23 (each 3H, s, aliphatic OAc), 1.960, 2.065, 2.072 (each 6H, s, aliphatic OAc), 2.33 (6H, s, aromatic OAc), 3.90 (3H, s, OMe), 4.37, 4.43, 4.64 (each 1H, d, J = 8 Hz, H-1 of Glc), 5.68 (1H, J = 3.5 Hz, H-1 of Glc-1), 6.28 (1H, d, J = 16 Hz, H-β of *p*-coum.), 6.51 (1H, d, J = 16 Hz, H-β of fer.), 7.07 (1H, d, J = 8 Hz, H-5 of fer.), 7.17 (1H, dd, J = 8, 1 Hz, H-6 of fer.), 7.18 (2H, d, J = 8.5 Hz, H-3, H-5 of *p*-coum.), 7.19 (1H, d, J = 2 Hz, H-2 of fer.), 7.49 (2H, t, J = 8 Hz, H-3, H-5 of benz.), 7.58 (2H, d, J = 8.5 Hz, H-2, H-6 of *p*-coum.), 7.61 (1H, tt, J = 8, 1 Hz, H-4 of benz.), 7.65 (1H, d, J = 16 Hz, H-γ of *p*-coum.), 7.78 (1H, d, J = 16 Hz, H-γ of fer.), 8.10 (2H, dd, J = 8, 1 Hz, H-2, H-6 of benz.). FAB-MS *m/z*: 1950 $[M+Na]^+$, 1928 $[M+H]^+$.

Alkaline Hydrolysis of 1—6 Each compound (2 mg) was treated with 2% NaOH aq. (3 drops) for 4 h at room temperature and the reaction mixture was passed through a column filled with Amberlite IR-120B. From the water eluate of the reaction mixture of **1—6** a pentasaccharide **1a** was detected by HPLC [Asahipak NH2P-50, 4.6 mm × 25 cm, CH_3CN–H_2O (65 : 35), 1.0 ml/min, UV 195 nm,[5] t_R 7.3 min], the retention time was identical to that of desacyl compound of senegose A.[1] From the methanol eluate of the reaction mixture of **1—4** benzoic, *p*-coumaric and ferulic acids, from that of **5** benzoic, *p*-coumaric and *cis*-ferulic acids and from that of **6** benzoic, *cis*-*p*-coumaric and ferulic acids were identified by HPLC [YMC R-ODS-7, 4.6 mm × 25 cm, CH_3CN–H_2O–trifluoroacetic acid (22.5 : 77.5 : 0.05), 1.0 ml/min, UV 270 nm, t_R 11.3 min (*p*-coumaric acid); 12.2 min (*cis*-*p*-coumaric acid); 12.6 min (ferulic acid); 12.9 min (*cis*-ferulic acid); 18.5 min (benzoic acid)].

Acid Hydrolysis of 1—6 A solution of each compound (2 mg) in 5% H_2SO_4 (3 drops) was heated in a boiling water bath for 30 min. The solution was passed through a column filled with Amberlite IRA-60E and the residue was concentrated. From **1—6**, glucose and fructose were detected in the ratio 4 : 1 by HPLC [Asahipak NH2P-50 4.6 mm × 25 cm, CH_3CN–H_2O (80 : 20), 1.0 ml/min, UV 195 nm, t_R 9.3 min (fructose); 12.2 min (glucose)].

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